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Published in:
Applied Physics Letters

DOI:
10.1063/1.122934

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Citation: Appl. Phys. Lett. **73**, 3914 (1998); doi: 10.1063/1.122934
View online: https://doi.org/10.1063/1.122934
View Table of Contents: http://aip.scitation.org/toc/apl/73/26
Published by the American Institute of Physics

Electrical characterization of electroluminescent polymer/nanoparticle composite devices

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(Received 29 July 1998; accepted for publication 21 October 1998)

The current–voltage characteristics of light-emitting devices containing thin films of poly(dialkoxy-*p*-phenylene vinylene) (PPV) incorporated with silicon dioxide nanoparticles have been investigated. It is demonstrated that the current enhancement of the devices containing composite layers can be modeled by assuming that the effective thickness of the composite layers is about half of their actual thickness. Field-effect measurements reveal that the mobility of the charge carriers in PPV is not significantly changed by the incorporation of nanoparticles. © *1998 American Institute of Physics.* [S0003-6951(98)03052-6]

Polymer light-emitting diodes (PLEDs) have been considered promising candidates for large-area applications as a result of both easy processing and mechanical flexibility.[1] The external conversion efficiency of poly(phenylene-vinylene) (PPV) -based light-emitting diodes (LEDs) amounts to 2% photons/charge carrier. Typically, for a light output of 100 cd/m^2 only a drive voltage in the range of 3–4 V is required for a PLED with a PPV layer thickness of about 100 nm. Recently, it has been demonstrated by Carter *et al.*[2] that mixing oxide nanoparticles into a PPV derivative gives rise to an enhancement of the current density and radiance in a PLED by more than an order of magnitude at low voltage. As a result, in these polymer/nanoparticle composite devices radiances of 10 000 cd/m^2 have been achieved at a drive voltage of only 5 V. For applications, the resulting gain in power efficiency in these composite devices is very attractive.

The mechanism for the current and radiance enhancement in a PLED is not yet fully understood. In earlier studies it has been demonstrated that the incorporation of nanoparticles in polymer layers can improve their electro-optic properties such as the photovoltaic efficiency[3,4] and lasing threshold.[5] However, as argued by Carter *et al.*,[2] the radiance increase is not due to microcavity effects resulting from the insulating oxide particles since there are no line-narrowing effects observed. Furthermore, since the radiance enhancement is independent on the refractive index of the nanoparticles, scattering effects can also be excluded. Finally, an increase of the recombination at a polymer/nanoparticle interface would result in an increased efficiency, which is not observed and cannot explain the current enhancement. Therefore, Carter *et al.* suggested that the current and radiance enhancement might arise from a change in the device morphology. A more rough cathode interface may give rise to an enhancement of the surface area with a resulting increase of electron injection.[2] Furthermore, the existence of thin spots created throughout the film by capillary forces would give rise to an increase of the electric field, enhancing the charge injection and/or charge transport.

Recently, we have presented a device model which describes the current and light output of PLEDs as a function of voltage. The key ingredients are that the hole current is space-charge limited[6] with a field- and temperature-dependent mobility,[7] the electron current is reduced by traps,[6] and finally, the recombination between the electrons and holes is of the Langevin type.[8] In the present study we apply this device model to the nanoparticles/polymer composite light-emitting devices in order to further investigate the mechanism of the current and radiance enhancement.

The light-emitting devices consist of a polymer layer sandwiched between two electrodes on top of a glass substrate. The polymer used in our study is a random copolymer of 2,5-bischloromethyl-4-methoxy-1-(3,7-dimethyloctyloxy)-benzene and 2,5-bischloromethyl-4′-(3,7-dimethyloctyloxy)-1,1′-biphenyl, as shown in the inset of Fig. 2. Fumed monodispersive SiO_2 nanoparticles (7 nm, obtained from Aldrich) were first treated with hexamethyldisilazane in CH_2Cl_2 at 40 °C for one day, evaporated, redispersed in toluene by ultrasonic treatment, and evaporated again. This treatment reduced water uptake by the particles and improved the stability of the dispersions. A concentrated dispersion (10% w/w), prepared in toluene by ultrasonic treatment, was then added to a polymer solution in the same solvent. This led to solutions with a concentration in polymer of 0.4%–0.55%, and a 2:1 weight ratio of polymer and nanoparticles. Just before use, the solution was again treated in an ultrasonic bath for 30–60 min and filtered on a membranefilter (5 μm, Teflon). A patterned indium–tin oxide (ITO) is used as a bottom electrode, which injects holes, whereas an evaporated Ca electrode is used as a top contact. The current density–voltage ($J-V$) measurements are performed in a nitrogen atmosphere at room temperature.

The experimental $J-V$ characteristics for devices with and without the SiO_2 nanoparticles are shown in Fig. 1. The thickness L of both devices amounts to 200 nm. Since the presence of nanoparticles effects the capacitance of the device, the thickness is determined with a Dektak 3030 surface profiler, which is a mechanical technique. In Fig. 2 the corresponding external quantum efficiencies are shown. Our results are in agreement with the results reported earlier in the literature:[2] Above the threshold for light-emission incorpora-

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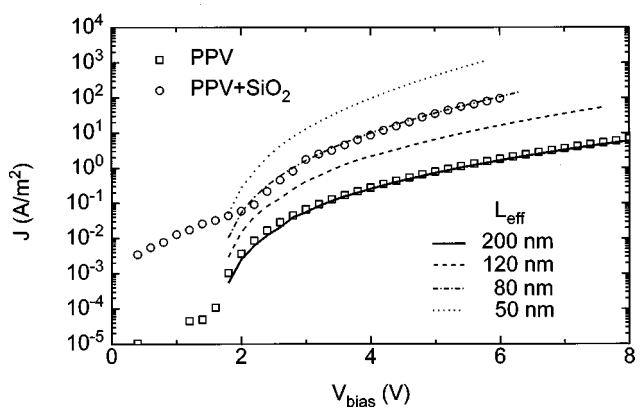

FIG. 1. Experimental $J-V$ characteristics at room temperature (symbols) for an ITO/PPV/Ca and a composite ITO/PPV–SiO_2/Ca light-emitting device both with a thickness of $L=200$ nm. Also shown are the calculated $J-V$ characteristics for a standard PPV-based LED with thickness L_{eff} for various L_{eff} (lines). The composite PLED with $L=200$ nm behaves identically as a standard PPV-based LED with a thickness of 80 nm.

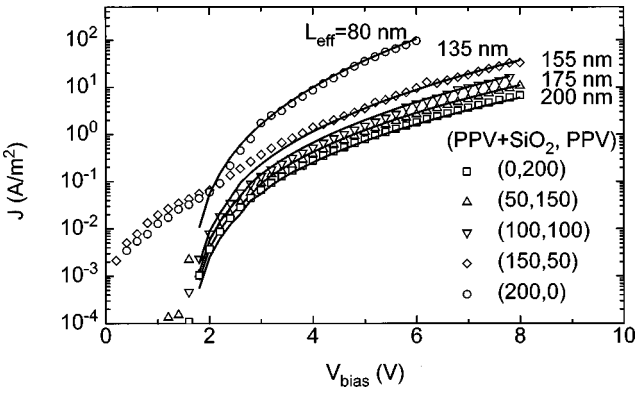

FIG. 3. Experimental $J-V$ characteristics at room temperature (symbols) for double-layer PLEDs consisting of a bottom layer of the composite PPV–SiO_2 covered with a standard PPV layer. The total thickness of both layers is kept constant at $L_{\text{tot}}=200$ nm. The thickness of the separate layers amounts to 0 (200) nm, 50 (150) nm, 100 (100) nm, 150 (50) nm, and 200 (0) nm, respectively. The double-layer devices can be modeled (solid lines) as a single-layer PPV-based LED with a thickness L_{eff} ranging from 80 to 200 nm.

tion of the nanoparticles gives rise to an enhancement of the current and radiance over an order of magnitude whereas the quantum efficiency is hardly affected.

In order to further investigate the observed effects we modeled the $J-V$ characteristics of the device without the nanoparticles as indicated by the solid line in Fig. 1. For this calculation a device model for a PLED is used, which has recently been presented:[8] The hole transport in our PLEDs with thickness L_{eff} is space-charge limited with a field-dependent mobility according to $\mu_p(E)=\mu_0 \exp(\gamma\sqrt{E})$ with a zero-field mobility $\mu_0=10^{-11}\,\text{m}^2/\text{V s}$ and a $\gamma=4.5\times10^{-4}(\text{m/V})^{1/2}$ at room temperature for this PPV derivative.[7] The electron transport is limited by traps[6] with a density of $5\times10^{23}\,\text{m}^{-3}$, and which are exponentially distributed in energy according to a characteristic temperature $T_t=1400$ K. The recombination between electrons and holes is governed by a bimolecular recombination constant which amounts[8] to $B=2\times10^{-12}\,\text{cm}^{-3}/\text{s}$. As shown in Fig. 1, our model using $L_{\text{eff}}=200$ nm is in good agreement with the experimental results for the device without nanoparticles. For comparison, the $J-V$ characteristics for PLEDs with layer thicknesses L_{eff} of 120, 80, and 50 nm have also been calculated. It appears that both the magnitude of the current density as well as the field dependence of a composite PLED with actual thickness $L=200$ nm are identical to the calculated $J-V$ characteristics of a device without nanoparticles with an effective thickness L_{eff} of 80 nm. Thus, addition of the nanoparticles not only increases the magnitude of the current but also its voltage dependence. Such a behavior is also expected for devices which have a thinner active layer.

The effect of a thickness reduction is further investigated by fabricating bilayer devices consisting of a bottom layer of composite PPV/SiO_2 and a top layer of standard PPV. The layer thicknesses of both the individual layers are changed, whereas the total thickness L_{tot} is kept constant at 200 nm. In Fig. 3 the $J-V$ characteristics of various devices are presented in which the thickness of the individual layers amounts to 0, 50, 100, 150, and 200 nm, respectively. Both the magnitude and field dependence of all these bilayer devices can be modeled using the standard parameters for PPV by just assuming that the effective thickness L_{eff} of the device has changed. As expected, L_{eff} is dependent on the fraction of the individual layer thicknesses of the standard (L_{PPV}) and composite PPV ($L_{\text{PPV+SiO}_2}$). In Fig. 4 the calculated L_{eff} from the $J-V$ characteristics of Fig. 3 are shown as

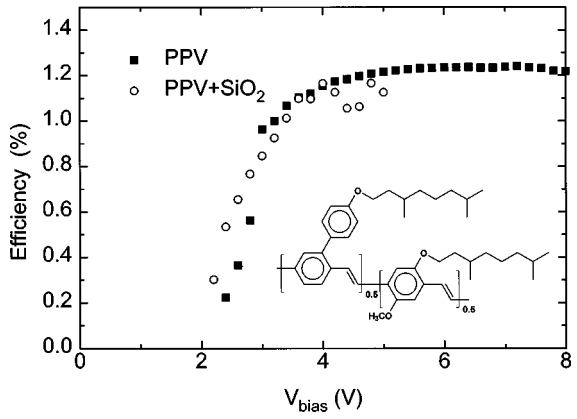

FIG. 2. External quantum efficiency (photons/charge carrier) as a function of applied voltage for a composite and standard PPV LED with thickness $L=200$ nm. The inset shows the PPV derivative used in this study.

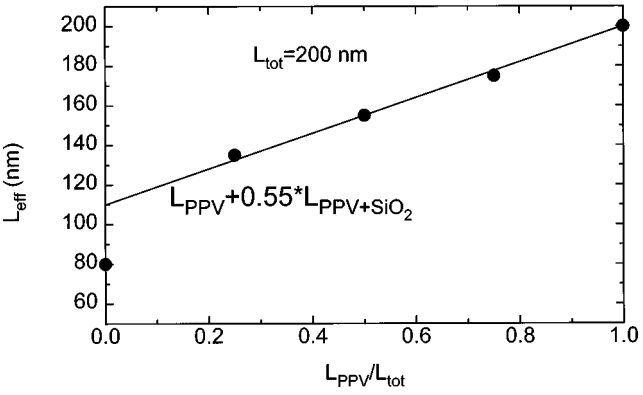

FIG. 4. L_{eff} as obtained from the model calculations on the $J-V$ characteristics of the double-layer devices (see Fig. 3) as a function of the fraction $L_{\text{PPV}}/L_{\text{tot}}$. The effective thickness L_{eff} of the composite PPV layers is about half of their actual thickness.

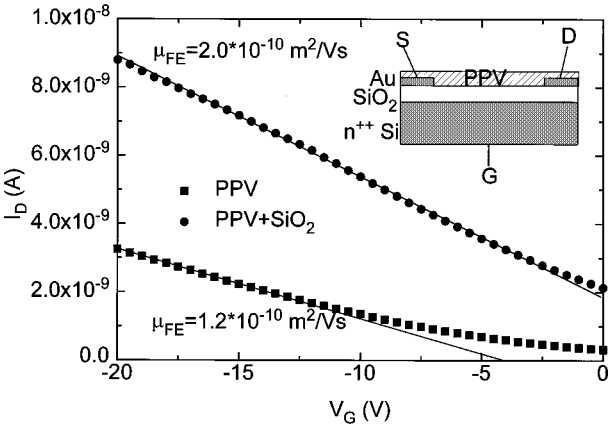

FIG. 5. Drain current I_D as a function of gate voltage V_G for the composite PPV–SiO_2 and standard PPV with a layer thickness $L=200$ nm measured at room temperature in air. The field-effect mobility amount to 2.0×10^{-10} and 1.2×10^{-10} $m^2/V\,s$, respectively.

a function of the fraction $L_{\mathrm{PPV}}/L_{\mathrm{tot}}$. It appears that for the bilayer devices L_{eff} follows the relation $L_{\mathrm{PPV}}+0.55\,L_{\mathrm{PPV+SiO_2}}$ (solid line). Thus, the composite layers electrically behave as standard layers which have about half of their thickness. Only the device with the single composite layer ($L_{\mathrm{PPV}}/L_{\mathrm{tot}}=0$) of 200 nm shows a stronger reduction of L_{eff} to 80 nm. A possible explanation for this deviation might be the fact that by covering the composite layer with another layer the roughness in the morphology due to the presence of nanoparticles might be slightly smoothened by the top layer.

In order to calculate L_{eff} from the experimental data in Fig. 3 we have assumed that in our device model the charge carrier mobility and its field dependence are not affected by the presence of nanoparticles. However, when the nanoparticles have a strong effect on, for example, the alignment of the polymer chains, a change in the charge carrier mobility could be expected. In that case, our calculation would not provide a correct estimation of L_{eff}. In order to clarify the effect of nanoparticles on the mobility, field-effect measurements have been performed. The structure, as indicated in the inset of Fig. 5, consists of a n^{++}-doped Si substrate which acts as a gate, a SiO_2 insulating layer, and interdigitated Au electrodes which are covered with the polymer.[9] In Fig. 5 I_D is shown as a function of the gate voltage V_G. The field-effect mobility can now be calculated in the linear regime[9] from the slope of I_D vs V_G. It appears that the hole mobility in the PPV/SiO_2 composite layer is only a factor of 1.7 larger as compared to the standard PPV. Thus, it is evident that the observed current enhancement of one order of magnitude as a result of the addition of nanoparticles does not originate from a mobility increase. Furthermore, the small difference in mobility has only a minor effect on the calculation of L_{eff} due to the strong dependence of the current on the layer thickness. As a result, the observed reduction of the effective layer thickness has a morphological origin, as suggested by Carter *et al.*[2] Clustering of nanoparticles may lead to inhomogeneities in the layer thickness and polymer density resulting in effective thin spots due to capillary forces.

In conclusion, we have demonstrated that the enhancement of the current and radiance in polymer/nanoparticle composite devices can be understood in terms of a reduced effective layer thickness. Both the magnitude and field dependence of the current are consistent with the assumption that electrically the effective thickness of a composite layer is about half of the actual thickness. Field-effect measurements reveal that the hole mobility in PPV is not significantly affected by the incorporation of nanoparticles. Thus, the incorporation of nanoparticles into an electroluminescent polymer opens the possibility to combine the advantages of thick layers as mechanical strength and improved substrate coverage with the favorable electro-optic properties of a thin device.

[1] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackey, R. H. Friend, P. L. Burn, and A. B. Holmes, Nature (London) **347**, 539 (1990).
[2] S. A. Carter, J. C. Scott, and P. J. Brock, Appl. Phys. Lett. **71**, 1145 (1997).
[3] N. C. Greenham, P. Xiaogang, and A. P. Alivisatos, Phys. Rev. B **54**, 17628 (1996).
[4] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, Science **270**, 1789 (1995).
[5] F. Hide, B. J. Schwartz, M. A. Diaz-Garcia, and A. J. Heeger, Chem. Phys. Lett. **256**, 424 (1996).
[6] P. W. M. Blom, M. J. M. de Jong, and J. J. M. Vleggaar, Appl. Phys. Lett. **68**, 3308 (1996).
[7] P. W. M. Blom, M. J. M. de Jong, and M. G. van Munster, Phys. Rev. B **55**, R656 (1997).
[8] P. W. M. Blom, M. J. M. de Jong, and S. Breedijk, Appl. Phys. Lett. **71**, 930 (1997).
[9] A. R. Brown, C. P. Jarrett, D. M. de Leeuw, and M. Matters, Synth. Met. **88**, 37 (1997).